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NMR Studies Part 4: Kraft Delignification Chemistry Structural Analysis of Residual Lignin

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Residual lignin from a series of softwood kraft pulps was isolated and structurally characterized by NMR. Results of these analyses showed that residual lignin structure differs depending upon the lignin content of the pulp and the pulping technology employed. The lower lignin content pulps had reduced contents of aliphatic hydroxyl groups and β-O-4 structures and higher contents of phenolic hydroxyl groups, carboxylic acid groups, and condensed structures compared to higher kappa number pulps. Analysis of residual lignins isolated from conventional kraft pulps (CK) and extended modified kraft pulps (EK) indicated that the CK pulps had lower contents of β-O-4 structures and higher contents of condensed structures. These differences potentially explain the improved delignification selectivity of EK kraft pulping because residual lignin with a higher content of β-O-4 structures and lower content of condensed structures would be more reactive under pulping conditions.

Introduction

The kraft pulping process is the dominant method of manufacturing high-value paper from wood in North America. Employing a combination of sodium hydroxide and sodium sulfide at high temperatures (ca. 170°C), lignin is effectively degraded into water-soluble fragments affording pulp fibers that are predominantly composed of cellulose and hemicellulose (Rydholm, 1965). Unfortunately, conventional kraft pulping technologies can only remove approximately 90-95% of the lignin in the fiber, and the

remaining lignin must be removed employing oxidative bleaching chemicals. Recently, the effluents from pulp bleaching operations have come under increasing societal and governmental concern (Grace et al., 1987). To minimize the effluent load from bleaching operations a renaissance in kraft pulping research has occurred.

Research studies by Sjoblom and Lindblad (1990) established the basic pulping parameters that could improve the delignification capabilities of conventional kraft pulping without detrimentally impacting strength properties. Process changes include leveling out the addition of NaOH, using a high charge of NaSH early in the cook, decreasing the amount of dissolved lignin during pulping, and lowering the overall cooking temperature (Jiang et *al.*, 1992). These modifications in pulping technology have been rapidly incorporated into commercial practice and, to some extent, have outstripped our fundamental knowledge of residual lignin structure (see Figure 1) from modern kraft pulping operations.

To address this issue, several research groups have begun to explore the nature of residual lignin after extended modified kraft pulping. A recent report by Hortling et *al.* (1992) indicated that extended delignification of softwood kraft pulp yielded a residual lignin that contained more condensed structures (see Figure 1) than that isolated from a conventional kraft cook.

Insert Figure 1

Jiang and Argyropoulous (1994) and Froass et *al.* (1996) noted that the content of β-O-aryl ether linkages in the residual lignin of a conventional kraft pulp was lower than that found in a modified kraft pulping process despite the fact that both pulps had comparable amounts

of lignin. This difference in β-O-aryl ether linkage content is significant because base-catalyzed cleavage of this structural component of lignin is one of the principal mechanisms involved in the depolymerization of lignin during pulping as shown in Figure 2.

Insert Figure 2

Additional studies are needed to define how changes in the pulping process influence the structure of residual lignin and its impact on subsequent bleaching operations. This paper examines the nature of residual lignin over a broad range of pulping conditions for conventional and extended modified kraft cooking processes.

Experimental Section

Materials. Chemicals used in this research were purchased from Aldrich, JT Baker, and EM Science and were used as received except for the dioxane, which was purified by distilling in the presence of $NaBH_4$ prior to use. Filtered Nanopure de-ionized (DI) water was used in all instances when water was required.

Wood Source and Chip Processing. The chips used for the pulping experiments were obtained from a fresh Loblolly Pine (*Pinus taeda*) tree that was cut in North Georgia, U.S.A. The wood was debarked, split, and chipped. The chips were then mixed and screened. The chips were screened by first collecting the fraction that passed though a 6-mm bar screen. The accepts were then screened on a ¼" mesh screen to remove all the small debris.

Kraft Pulping. Conventional (CK) and simulated Extended Modified Continuos Cooking: EMCC® (EK) pulping studies were performed by Ahlstrom Machinery in Glens Falls, NY. Conventional pulping was performed by charging all the NaOH and NaSH (white liquor) in the beginning of the cook. Simulated EK pulping was performed following established procedures involving various additions of white liquor (Jiang, 1992). EK pulping was started by adding white liquor and impregnating the chips for 30 minutes at 110°C and ~1000 kPa. The co-current cooking stage began after this impregnation stage by adding another charge of white liquor and raising the temperature to the maximum cooking temperature. Counter-current cooking was simulated by adding weak white liquor while simultaneously extracting black liquor at a similar flow rate to maintain a desired profile of alkali and dissolved lignin concentration. The pulping conditions employed to manufacture these pulps and some of the final properties of the pulps are summarized in Table 1.

Table 1. Relevant pulping conditions and pulp properties for the CK and EK kraft pulps.

	CK			EK		
Pulp ID	**C28**	**C18**	**C13**	**E29**	**E18**	**E14**
WL sulfidity, % AA[1]	27.4	27.4	27.4	27.4	27.4	27.4
Initial EA, % NaOH	19.7	19.7	22.0	12.0	12.0	12.0
Co-current EA[2] %	-	-	-	5.0	5.0	5.0
Counter-current EA %	-	-	-	4.4	4.2	5.0
L/W ratio	4.0	4.0	4.0	4.0	4.0	4.0
Max. temp, °C	170	170	170	158	161	169
H-factor	1715	2601	4238	1651	2229	4238
Kappa number	28.0	18.5	13.0	29.1	18.5	14.5
Viscosity, mPa.s	33.6	17.5	10.9	51.8	35.4	18.1
Viscosity/Kappa # ratio	1.20	0.95	0.84	1.78	1.91	1.25
Screened yield, %	45.9	42.8	41.0	45.6	43.8	40.9

[1]WL:white liqour; AA:active alkali; [2]EA:effective alkali.

Residual Lignin Isolation. The pulps were extracted with acetone for 24 hours in a Soxhlet extractor, washed thoroughly with de-ionized water, and air dried prior to isolating the residual lignin. The air dried pulp was placed in a round-bottom flask diluted with 0.05 N HCl 9:1 dioxane:water yielding a final consistency of 4%.

After refluxing the pulp slurry for 1 h under argon, the mixture was cooled, and filtered. The filtrate was neutralized with sodium bicarbonate and filtered and worked-up following Gellerstedt and Lindfors (1991) methods (see Table 2 for lignin yields).

NMR Spectroscopy. All NMR spectra were recorded on a Bruker 400 MHz DMX NMR spectrometer.

^{13}C-NMR Spectroscopy. ^{13}C-NMR spectra were recorded under quantitative conditions using an inverse-gated pulse sequence with a $\pi/2$ pulse and a 10-sec delay (Robert, 1992) and a sweep width of 330 ppm. All experiments employed 300-400 mg lignin/ml of $DMSO_{d6}$ and were recorded at 50°C. The FIDs were FT processed with 10 Hz line-broadening and analyzed according to reported chemical shifts for lignin functional groups (Nimz, et *al.*, 1982; Kringstad and Morck, 1983). Lignin spectra were integrated, and the area of the aromatic signals was assigned a value of 6. (Robert, 1992).

^{31}P NMR Spectroscopy. Lignin samples were phosphorlyated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane following the procedure of Granata and Argyropoulous (1995) and analyzed by ^{31}P-NMR.

Table 2. Sample abbreviations and residual lignin yields from acid hydrolysis procedure.

Pulp Description	Sample Abbreviation Pulp & Residual Lgnin (r.l.)		Yield of Lignin from Acid Hydrolysis
CK 28.0 kappa[1]	C28	C28 r.l.	35%[2]
CK 18.5 kappa	C18	C18 r.l.	38
CK 13.0 kappa	C13	C13 r.l.	45
EK 29.1 kappa	E29	E29 r.l.	33
EK 29.1 kappa	E29	E29 r.l.'[3]	28
EK 18.5 kappa	E18	E18 r.l.	32
EK 14.5 kappa	E14	E14 r.l.	39

[1]kappa number is an indirect measurement of the lignin content of the pulp, mass% lignin content of a pulp = kappa # x 0.15%: [2]values in brackets are the isolated yield of lignin from the acidic dioxane procedure. Yield = grams lignin isolated/{0.15% x gr of pulp extracted(pulp kappa # before extraction-pulp kappa # after extraction)}; [3]sample E29r.l' was a repeat acid hydrolysis of E29 pulp.

Results and Discussion

A series of conventional kraft pulps and extended modified kraft pulps were produced from Loblolly pine wood chips under stimulated mill conditions. After each cook, the pulp was thoroughly water-washed, air-dried, and then extracted with an acidic dioxane solution (Gellerstedt and Lindfors 1984a). Tables 1 and 2 summarize some of the physical properties of the pulps and the yield of residual lignin isolated from the pulps, respectively.

The isolated lignin samples were characterized employing quantitative ^{13}C NMR. Additionally, lignin samples were phosphorlyated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and the derivatives were characterized by ^{31}P NMR (Faix et al., 1994). Figures 3 and 4 provide representative spectral data for the lignin samples that were isolated in this study.

Insert Figure 3 & 4

The NMR methods employed in this paper facilitated the characterization of some of the most important functional groups present in lignin, including phenoxy, condensed lignin, carboxylic acids, and aliphatic hydroxy groups. Changes in the relative proportions of these functional groups provide critical information on the nature of the reactions involved in modern pulping operations (Gellerstedt and Gustafsson, 1987). The following discussion attempts to evaluate how these functional groups change in kraft pulps depending upon the pulping technology employed and the level of residual lignin remaining in the pulp.

Aliphatic Hydroxyl Content. Figure 5 is a plot of the aliphatic hydroxyl content of the residual lignins isolated in this study plotted against the kappa number of the pulp from which the lignins were isolated. These results indicate that the residual lignins of both CK and EK pulps are significantly reduced in the aliphatic hydroxyl content as delignification proceeds.

Insert Figure 5

The replicates of C28 r.l. and E29 r.l. validate the reproducibility of the analytical techniques employed in this study. The aliphatic hydroxyl content of lignin is mainly comprised of primary and secondary hydroxyl groups located on C-γ and C-α of the phenylpropane side chain of lignin (see Figure 1). The loss in aliphatic hydroxyl groups can be attributed, in part, to the loss of the primary hydroxyl group of the phenyl propane chain as formaldehyde (Grierer, 1970) during the pulping process as shown in Figure 6.

Insert Figure 6

Figure 5 also suggests that the CK residual lignins had lower contents of aliphatic hydroxyl groups at 28 and 18 kappa numbers compared with EK residual lignins at similar kappa numbers. The degree to which lignin is modified during kraft pulping is presumably related to the content of aliphatic hydroxyl groups; hence, the CK residual lignin has undergone a more severe modification at a given kappa number.

Phenolic Hydroxyl Content. The phenolic hydroxyl group is an important functional group in lignin that substantially influences pulping and bleaching chemistry. Phenolic groups assist in the dissolution of lignin during pulping by aiding in the lignin's solubility in alkaline medium, and are involved in the formation of reactive quinone methide intermediates (Gellerstedt et al., 1988). Native wood lignin contains a low content of such groups, but during kraft delignification, the cleavage of aryl ether linkages creates new phenolic groups (see Figure 2). As a result, dissolved and residual lignins have a greater quantity of phenolic groups than native wood lignin (Grierer, 1980).

Characterization of the phenoxy content of residual kraft lignins was readily accomplished by phophorlyation and ^{31}P NMR analysis. ^{31}P-NMR analysis not only measures total phenoxy content but distinguishes between guaiacyl and C5-substituted ('condensed') phenolic groups. Figures 7 and 8 are plots of the total phenolic and condensed phenolic content versus the unbleached kappa number for the residual lignins isolated.

Insert Figures 7 & 8

A clear trend toward increasing phenolic contents as delignification proceeds is observed in these figures. The phenolic hydroxyl content of CK lignins increased as the kappa number was decreased from 29 to 18 and further delignification did not result in any further increase, rather the phenolic content appeared to level off. Under EK pulping conditions, a relatively minor increase in phenolic content is observed as the kappa number is lowered from 28 to 18, but a dramatic increase is observed as the kappa number is lowered to 14.

The observation that the content of phenolic hydroxyl groups is increasing with decreasing kappa number implies that the residual lignin is still undergoing cleavage of the remaining aryl ether linkages. The leveling off of the phenolic content in the CK residual lignins suggests that additional aryl ether cleavage is minimal, while the increase in the EK residual lignins indicates that additional aryl ether cleavage is still occurring.

Carboxylic Acid Content. The carboxylic acid content of the residual lignins was determined by ^{31}P-NMR. Figure 9 shows that residual lignin contains an increasing amount of carboxylic acid groups as

delignification proceeds. Interestingly, both EK and CK residual lignin appear to undergo a similar increase in the carboxylic acid content. ^{13}C NMR analysis of the samples leads to comparable conclusions with respect to changes in the acid content for residual lignin samples

Insert Figure 9

β-O-4 Aryl Ether Content. The contents of β-O-4 structures in the residual lignins were conveniently measured by ^{13}C-NMR. Although this could be accomplished by integrating the signal intensity of the β-O-carbon, this signal (δ90 - 78 ppm) is rather broad, and it is easier to integrate the Cγ in β-O-4 structures centered at ~60 ppm. The results of this analysis are plotted in Figure 10. This analysis indicates that the content of β-O-4 structures diminishes in both CK and EK residual lignins as the unbleached kappa number is decreased. The EK residual lignins were found to have a slightly greater content of β-O-4 structures compared with CK residual lignins at comparable kappa numbers.

Insert Figure 10

The cleavage of β-O-4 structures degrades lignin into smaller units and generates free phenol units. These fragmented lignin polymers are more reactive and soluble under kraft pulping conditions than native lignin. During kraft delignification, the content of β-O-4 structures is greatly reduced as seen from the data here and from that of others (Gellerstedt and Lindfors 1984; Kringstad and Morck, 1983). The

decreasing content of β-O-4 structures provides additional credence to increasing phenolic content being a result of additional β-O-4 cleavage.

The observation that there remains a detectable amount of β-O-4 structures even in the very low kappa residual lignin, after prolonged high temperature alkaline treatment, is somewhat remarkable. The data from Figure 10 suggest that the content does not approach a minimal level of β-O-4 structures, as would be expected if some β-O-4 structures were resistant to cleavage. Instead, it appears that there is a continual, steady decrease in the content of these structures, indicating that cleavable β-O-4 linkages remain even in the 13 kappa residual lignin.

Condensed Structures. Condensed lignin structures is the term used to describe lignin that has an aryl or alkyl substituent at the C5 and/or C6 position of the aromatic ring. Native wood lignin has some condensed-type structures such as the 5-5, β-5, β-1, and 4-O-5 structures (see Figure 1). Evidence for the formation of additional condensed structures during kraft pulping has also been suggested (Kringstad and Morck, 1983; Gellerstedt and Robert, 1987; Greier, et al., 1976). Condensed structures are stable under kraft delignification conditions and are therefore believed to be enriched in the residual lignin of kraft pulp causing the residual lignin to be unreactive.

The content of condensed structures in residual lignins has been estimated by ^{13}C-NMR. Substituted aromatic carbons have ^{13}C-NMR chemical shifts in the range of δ 160 to 123 ppm (Robert, 1992). Integrating this region in the ^{13}C-NMR spectra of residual lignin allows for the quantitative determination of substituted aromatic carbon atoms.

Figure 11 is a plot of the substituted aromatic content versus the unbleached kappa number for EK and CK residual lignins.

Insert Figure 11

This analysis shows that as the kappa number is decreased the residual lignins contain more substituted aromatic rings. The figure also shows that the EK residual lignins have less substituted aromatic rings than CK residual lignins at comparable kappa numbers. Whether these condensed structures are formed during pulping or are enriched in the residual lignin by the selective dissolution of uncondensed lignin during pulping can not be elucidated from this analysis.

Insert Figure 11

Gellerstedt and Gustafsson (1987) have found that for flow-through kraft pulping studies the lignin going into solution at the end of the cook is more condensed than the lignin being dissolved early during the cook, suggesting there is a selective dissolution of uncondensed lignin. The selective dissolution of uncondensed lignin may be causing the residual lignin to become more condensed as pulping is prolonged.

Conclusions

Structural analysis of CK and EK residual lignins isolated from pulps with different kappa numbers has revealed some significant differences in the structure of these residual lignins. As delignification proceeds, there is a decrease in aliphatic hydroxyl groups, an increase in phenolic hydroxyl groups, an increase in carboxylic acid groups, a

decrease in β-O-4 structures, and an increase in condensed structures. These differences are significant considering that the difference in kappa number between these pulps was approximately 15 units. The significant changes occurring as delignification is prolonged, such as the diminishing content of β-O-4 structures and the increasing content of condensed structures, would seemingly promulgate the unreactive nature of the residual lignin toward pulping chemicals. The low content of cleavable β-O-4 structures and the high content of alkali-stable condensed aromatic structures in lower kappa number pulps hinders the ability of this lignin to be further fragmented and dissolved. The poor selectivity of kraft pulping can therefore be partly attributed to the unreactive nature of residual lignin.

Structural differences between the CK and EK residual lignins at comparable kappa numbers were found that explain, in part, the improved delignification selectivity of EK pulping. At comparable kappa numbers, the EK residual lignins had a higher content of β-O-4 structures and a lower content of condensed aromatic structures, which would indicate that EK residual lignins would be more reactive toward the delignification conditions.

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Figure 1. Typical interunit lignin[a] linkages present in softwood.

[a]structures such as 5-5 and diphenylmethane are frequently referred to as condensed lignin structures.

Figure. 2: Cleavage of mechanism of β-O-4 aryl ether linkages in lignin

during kraft pulping.

Figure 3. Typical ^{31}P NMR spectral data for phosphylated residual lignin acquired from sample C28 r.l.

Figure 4. Typical ^{13}C NMR spectral data for C28 r.l.

Figure 5. Aliphatic hydroxyl content versus unbleached kappa number for CK (including four replicates of C28 r.l.) and EK residual lignins as determined by ^{31}P-NMR.

Figure 6. Loss of γ-carbon during kraft pulping.

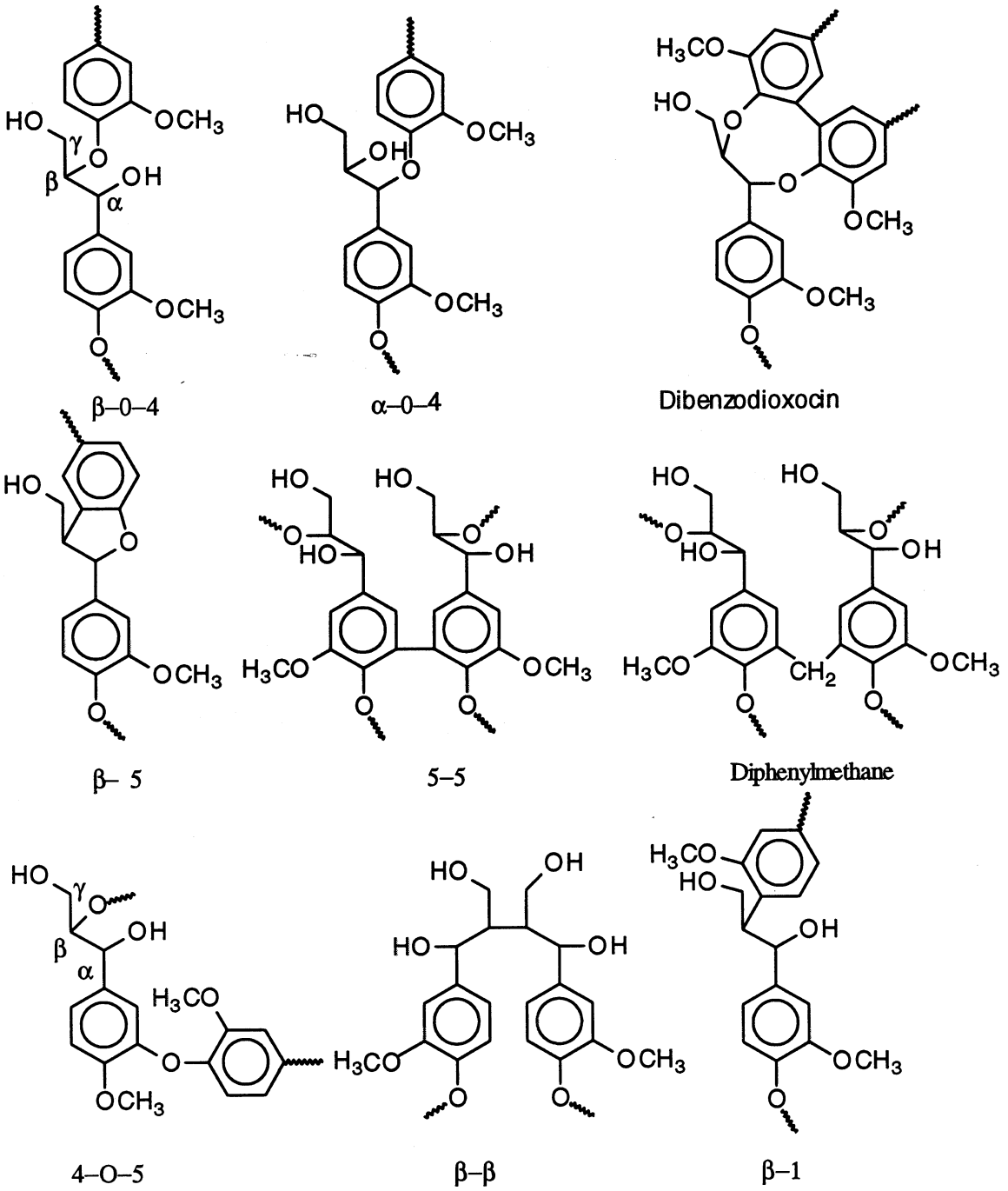
Figure 7. Total phenolic hydroxyl content versus unbleached kappa number for CK (including four replicates of C28 r.l.) and EK residual lignins as determined by ^{31}P-NMR.

Figure 8. Condensed phenolic hydroxyl content versus unbleached kappa number for CK (including four replicates of C28 r.l.) and EK residual lignins as determined by ^{31}P-NMR.

Figure 9. Carboxylic acid content versus unbleached kappa number for CK (including four replicates of C28 r.l) and EK residual lignins as determined by ^{31}P-NMR.

Figure 10. Content of Cγ in β-O-4 structures (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for CK and EK residual lignins as determined by quantitative ^{13}C-NMR spectra.

Figure 11. Content of substituted aromatic carbon atoms (expressed as number of C atoms per aromatic unit) versus unbleached kappa number for CK and EK residual lignins as determined by ^{13}C-NMR.



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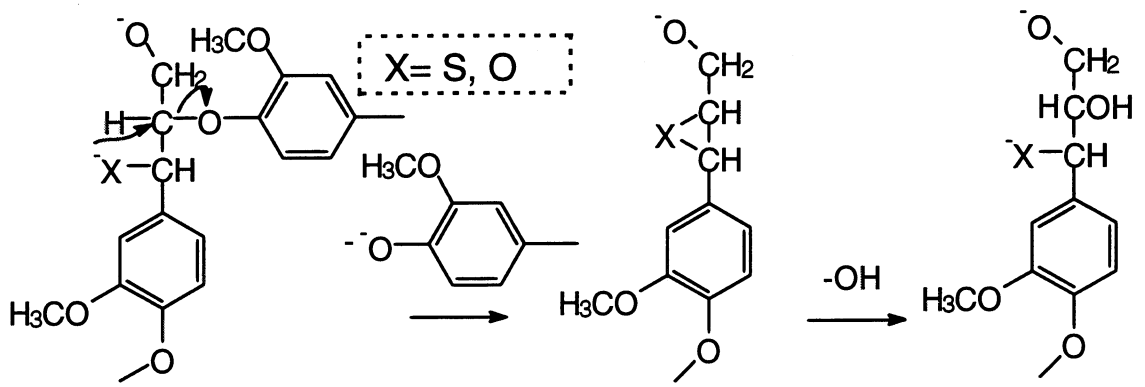

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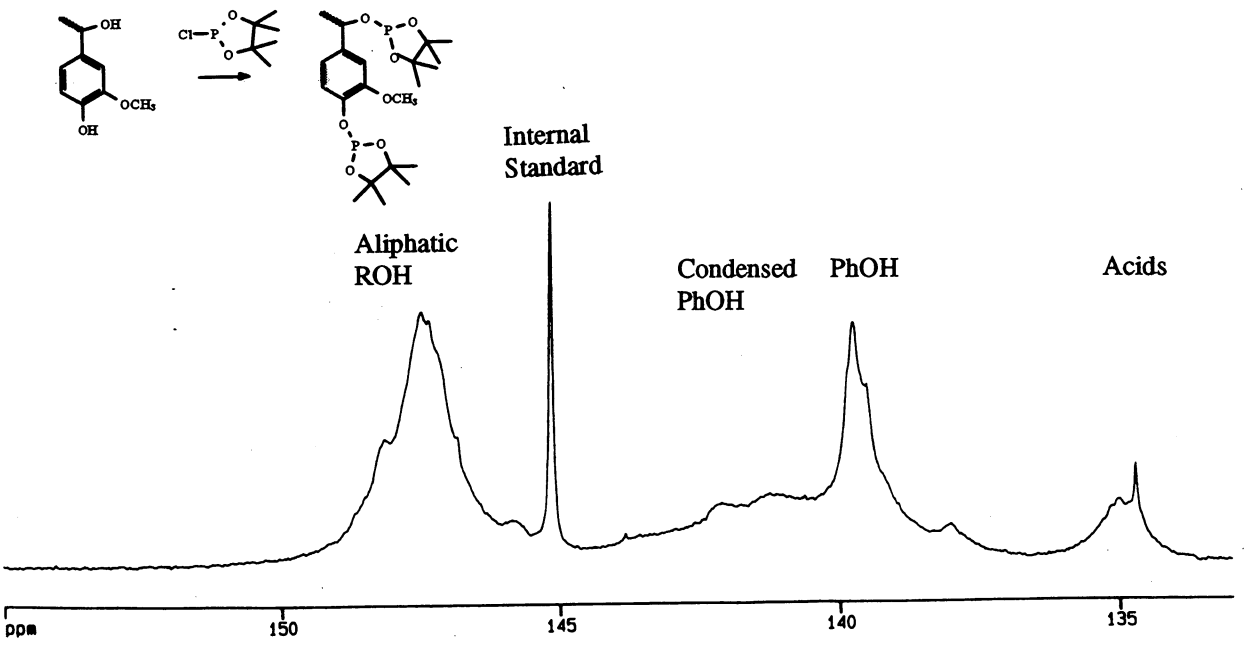
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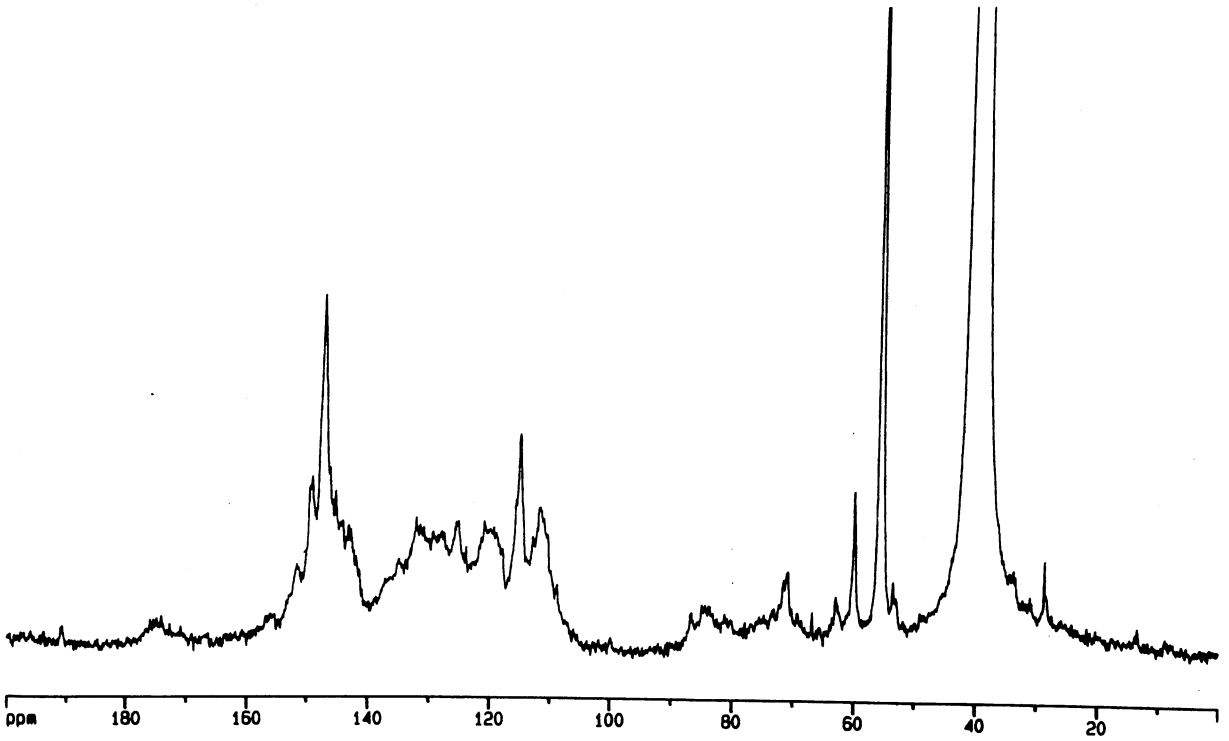
Figure 3.



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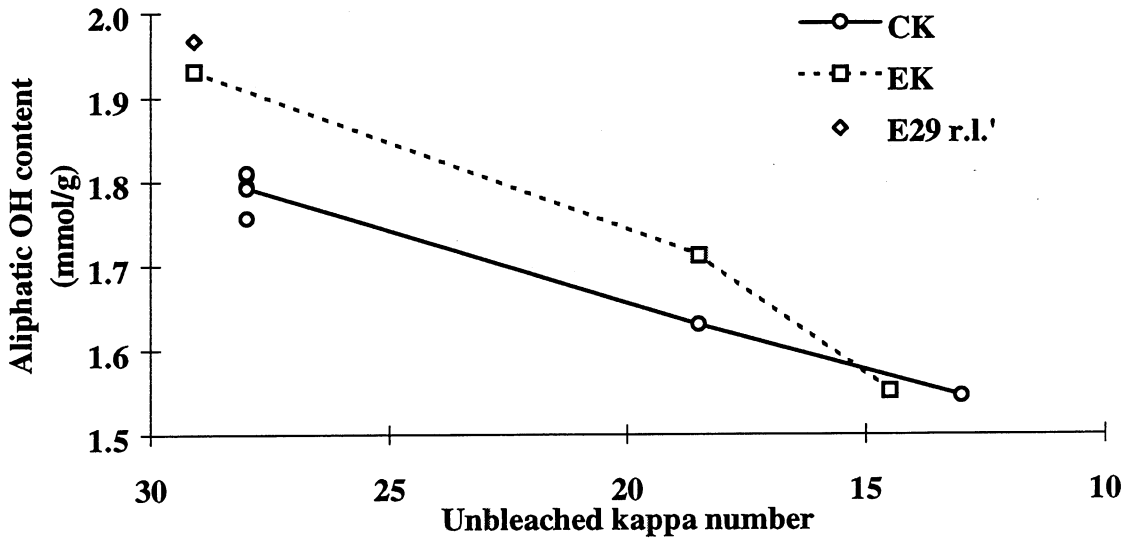
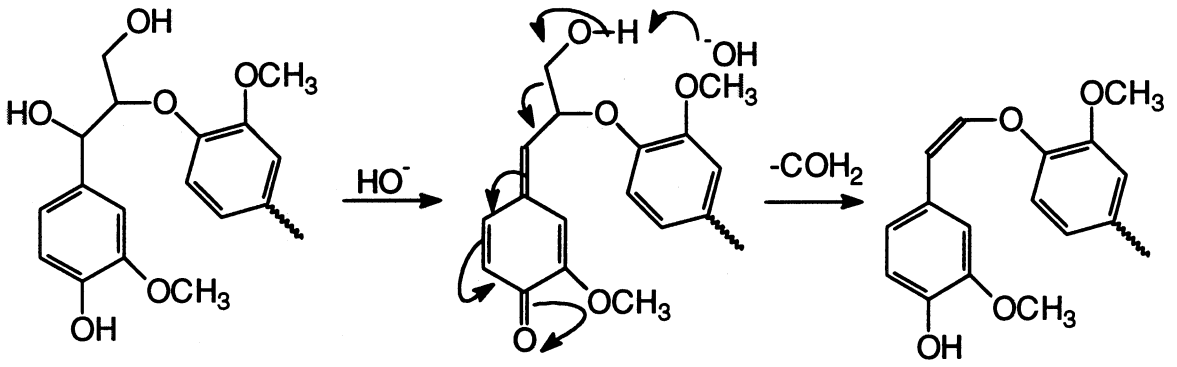

2.0
1.9
1.8
1.7
1.6
1.5
Aliphatic OH content (mmol/g)
30
25
20
15
10
Unbleached kappa number
CK
EK
E29 r.l.'

Figure 5.



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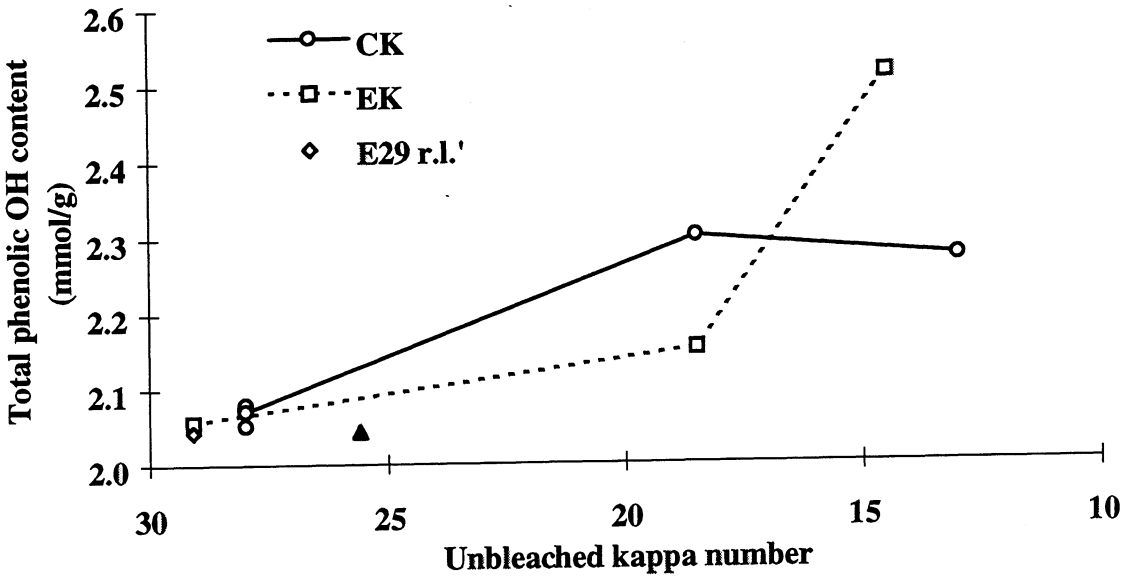
2.6
2.5
2.4
2.3
2.2
2.1
2.0
Total phenolic OH content (mmol/g)
CK
EK
E29 r.l.'
30
25
20
15
10
Unbleached kappa number

Figure 7.

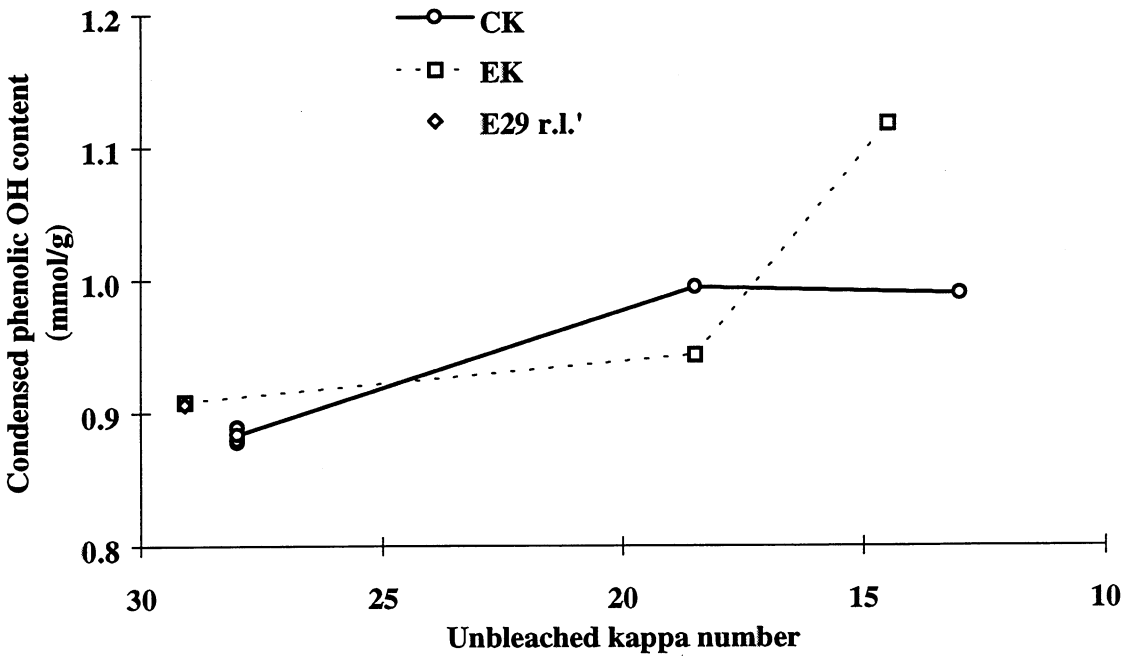
CK
EK
E29 r.l.'
Condensed phenolic OH content (mmol/g)
1.2
1.1
1.0
0.9
0.8
30
25
20
15
10
Unbleached kappa number

Figure 8.

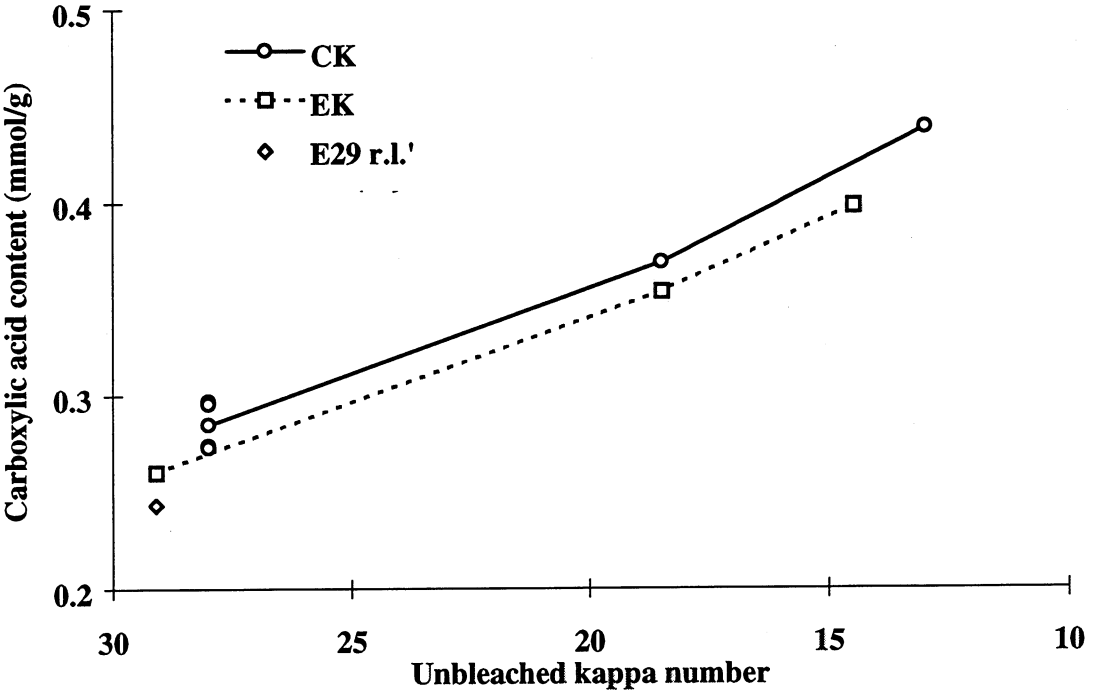
0.5
0.4
0.3
0.2
Carboxylic acid content (mmol/g)
CK
EK
E29 r.l.'
30
25
20
15
10
Unbleached kappa number

Figure 9.

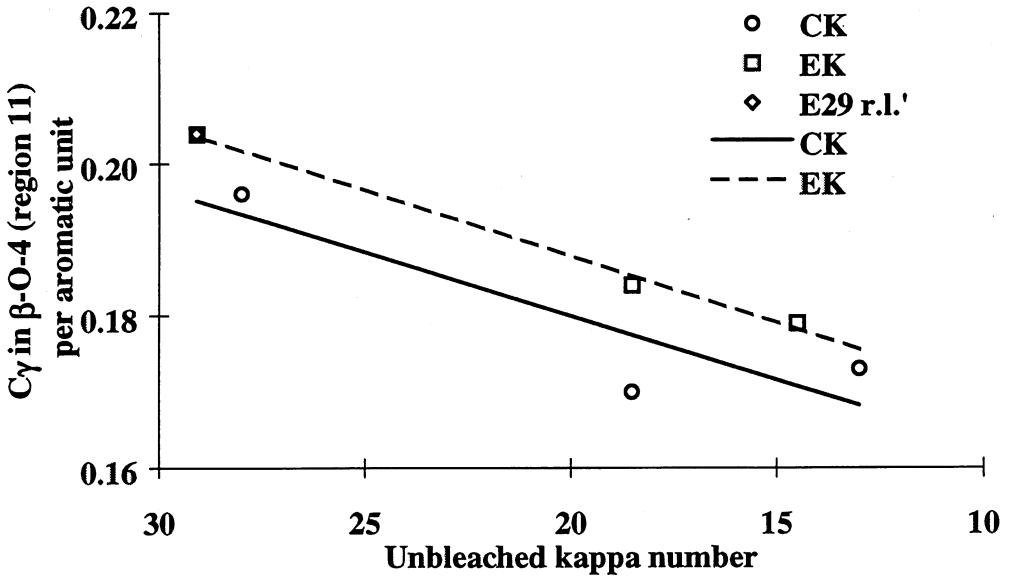
0.22
0.20
0.18
0.16
Cγ in β-O-4 (region 11)
per aromatic unit
30
25
20
15
10
Unbleached kappa number
CK
EK
E29 r.l.'
CK
EK

Figure 10.

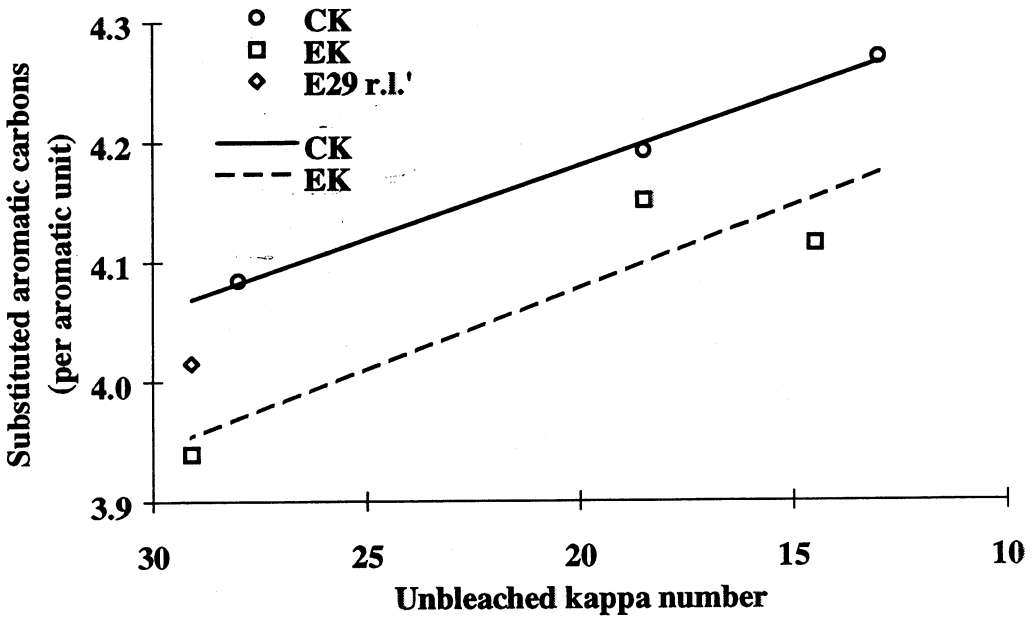
CK
EK
E29 r.l.'
CK
EK
Substituted aromatic carbons
(per aromatic unit)
4.3
4.2
4.1
4.0
3.9
30
25
20
15
10
Unbleached kappa number

Figure 11.